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Synthesis of bimodal molecular weight distribution polyethylene with α-diimine nickel(II) complexes containing *unsym*-substituted aryl groups in the presence of methylaluminoxane

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Abstract

A series of unsymmetrical complexes of 2,3-bis(2-phenylphenyl)-butanediimine nickel(II) dibromide (complex **1**), 1,4-bis(2-isopropyl-6-methylphenyl)-acenaphthenediimine nickel(II) dibromide (complex **2)** and *meso*- and *rac*-1,4-bis (2,4-di-*tert*-butyl-6-methylphenyl)-acenaphthenediimine nickel(II) dibromide (*meso*-**3** and *rac*-**3**) were synthesized and activated by methylaluminoxane (MAO) for ethylene polymerization. By ^{13}C NMR characterization, *meso*- and *rac*-stereo-isomers were detected in the condensation products resulting from the reaction of *unsym*-substituted anilines with diketones. It was notable that *meso*- and *rac*-isomers in ligand **1** or ligand **2** could not be separated owing to their interconversion, however, *meso*- and *rac*-isomers in ligand **3** could be isolated and identified by X-ray diffraction and NMR analysis. At low polymerization temperatures, complex **1**/MAO afforded polyethylene with bimodal molecular weight distribution, while complex **2**/MAO prepared polyethylene with single-modal distribution. Moreover, by raising polymerization temperature or extending time of catalyst aging, bimodal molecular weight distribution polyethylene was also produced by complex **2**/MAO. The hypothesis of bimodal molecular weight distribution polyethylene synthesized by unsymmetrical α-diimine nickel(II) complexes was supported that the molecular weight of polyethylene produced by *rac*-**3**/MAO was significantly higher than that produced by *meso*-**3**/MAO under identical polymerization conditions. A unique methodology to prepare polyethylene with bimodal molecular weight distribution was demonstrated.

Keywords: Unsymmetrical α-diimine nickel(II) complexes; Polyethylene; Methylaluminoxane; Bimodal molecular weight distribution; Stereo-isomers

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1. Introduction

Polyethylene with bimodal molecular weight distribution (MWD) has especially attractive

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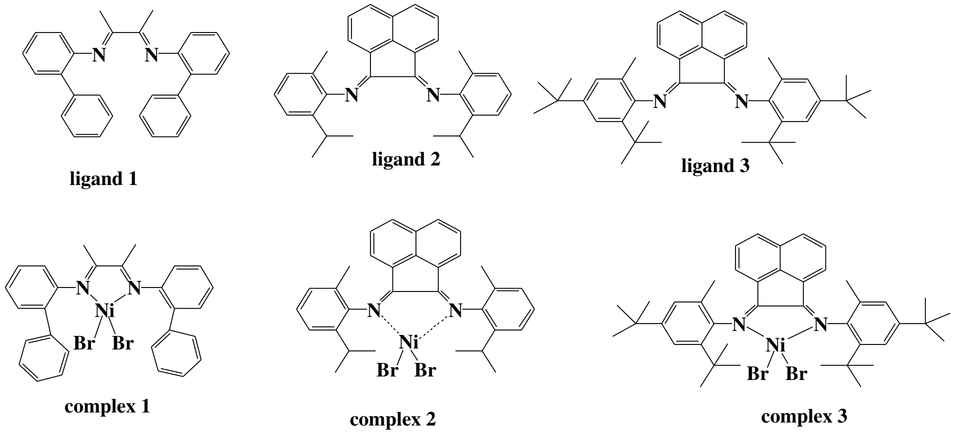


Scheme 1. Complex **1**, complex **2**, complex **3** and their corresponding unsymmetrical α-diimine ligands of ligand **1**, ligand **2**, ligand **3.**

mechanical and rheological properties. Although the use of the polyethylene is expected to increase, there are very few studies available to quantify MWD bimodality. In order to obtain bimodal molecular weight distributions polyethylene, several methods are available. It can be summarized as: stepwise polymerization in tandem reactor [1,2], polymerization of using mixtures of different catalysts [3–7], using binuclear catalysts or catalysts with special ligands [8–10], or using iron catalysts [11,12].

That α-diimine nickel(II) complexes with sterically bulky ligands were used as catalysts for ethylene polymerization to get high molecular weight polyethylene was a milestone in the development of homogeneous ethylene polymerization catalysts [13]. Currently, well-defined catalysts based on nickel complexes have been reported to polymerize ethylene [14–18]. Symmetrical α-diimine nickel(II) complexes afford single active species for ethylene polymerization to synthesize polyethylene with narrow and single-modal molecular weight distribution. What is about unsymmetrical α-diimine nickel(II) complexes? Pellecchia [19] and Coates [20,21] found that when α-diimine nickel complexes contain *unsym*-substituted aryl groups, they should have both *meso*- and *rac*-stereo-isomers. They used these unsymmetrical α-diimine nickel complexes to catalyze propylene polymerization and obtained much less stereoregular polypropylenes with respect to symmetrical α-diimine nickel(II) complexes. Relative to symmetrical α-diimine nickel(II) complexes, these systems have the potential to afford two active species with different steric bulk for ethylene polymerization and yield polyethylene with bimodal or broad molecular weight distribution. However, to the best of our knowledge, there have been few reports on the synthesis of bimodal molecular weight distribution polyethylene by using unsymmetrical α-diimine nickel(II) complexes.

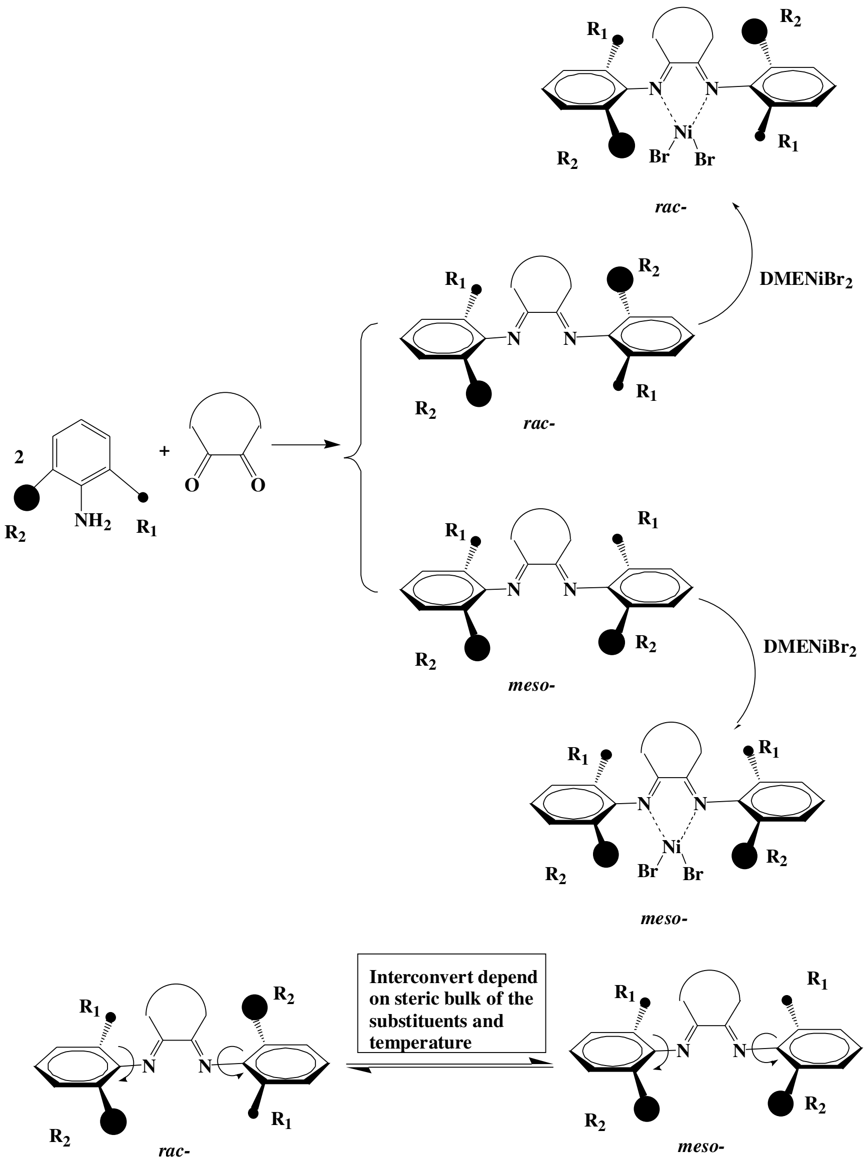
In this paper, as a follow up to our initial paper [22,23], complex **1, 2** and *meso*- and *rac*-isomers in complex **3** (*rac*-**3** and *meso*-**3**), as shown in Scheme 1, were synthesized and activated by MAO for ethylene polymerization, respectively. The molecular weight and microstructure of the resultant polyethylene were characterized by GPC and ^{13}C NMR.

2. Results and discussion

2.1. Synthesis and characterization of α-diimine nickel (II) complexes

The unsymmetrical α-diimine ligands were synthesized by condensation reaction of diketone with 2 equiv of unsym-substituted aniline, as detailed in Section 4. Compared with symmetrically α-diimine [14], there should be both *meso*- and *rac*-isomers in unsymmetrical α-diimine products as shown in Scheme 2. The two isomers could interconvert owing to rotation of the aromatic ring, and the conversion rate depended on steric bulk of the substituents. Ligand 2 was prepared by the reaction of 2-isopropyl-6-methylaniline with acenaphthene, and resulted in both *meso*- (~80%) and *rac*- (~20%) stereo-isomers existing in the condensation product determined by NMR. As evidenced by ^{13}C NMR in Fig. 1, two isomers in ligand **2** could interconvert. Therefore, it was difficult to isolate two isomers by column chromatography.

For ligand **3**, based on ^{13}C NMR characterization, the product of condensation reaction of 2,4-di-*tert*-butyl-6-methylaniline with acenaphthenequinone



Scheme 2. Synthesis of unsymmetrical α-diimine nickel(II) complexes.

was confirmed to be a mixture of *meso*- and *rac*-isomers, and they could not interconvert because of the sterically bulky substituent on aromatic ring. In this case, *meso*- and *rac*-isomers could be isolated by column chromatography and identified by X-ray diffraction and NMR analysis. As shown in Fig. 2, the first eluted isomer was *rac*-isomer with a crystallographic C_2 symmetry, while the second eluted isomer was *meso*-isomer with a crystallographic C_s symmetry. In Fig. 3, the ^{13}C NMR characteristic chemical shifts of *meso*-isomer are 34.8 (p-$C(CH_3)_3$), 33.6 (o-$C(CH_3)_3$), 30.8 (p-$C(CH_3)_3$), 29.3 (o-$C(CH_3)_3$) ppm, and ones of *rac*-isomer are 35.1 (p-$C(CH_3)_3$), 33.7 (o-$C(CH_3)_3$), 30.9 (p-$C(CH_3)_3$), 29.5 (o-$C(CH_3)_3$) ppm.

Complex **2** containing both *meso*- and *rac*-isomers was readily obtained from the reaction of corresponding α-diimine ligand **2** which was a mixture of *meso*- and *rac*-isomers with (DME)NiBr$_2$. *Meso*- or *rac*-isomer of 1,4-bis (2,4-di-*tert*-butyl-6-methylphenyl)-acenaphthenediimine nickel(II) dibromide (complex **3**), which were named *meso*-**3** and *rac*-**3**, was respectively synthesized by the reaction of corresponding *meso*- or *rac*-α-diimine ligand with (DME)NiBr$_2$.

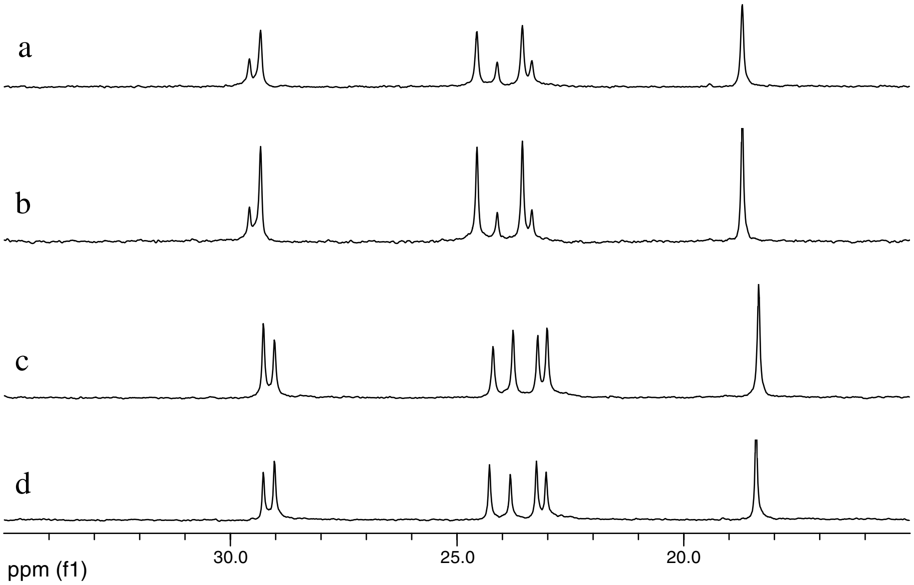


Fig. 1. ^{13}C NMR spectra of α-diimine ligands **2** at 25 °C with different time a (4 h), b (11 h), c (48 h), d (10 day).

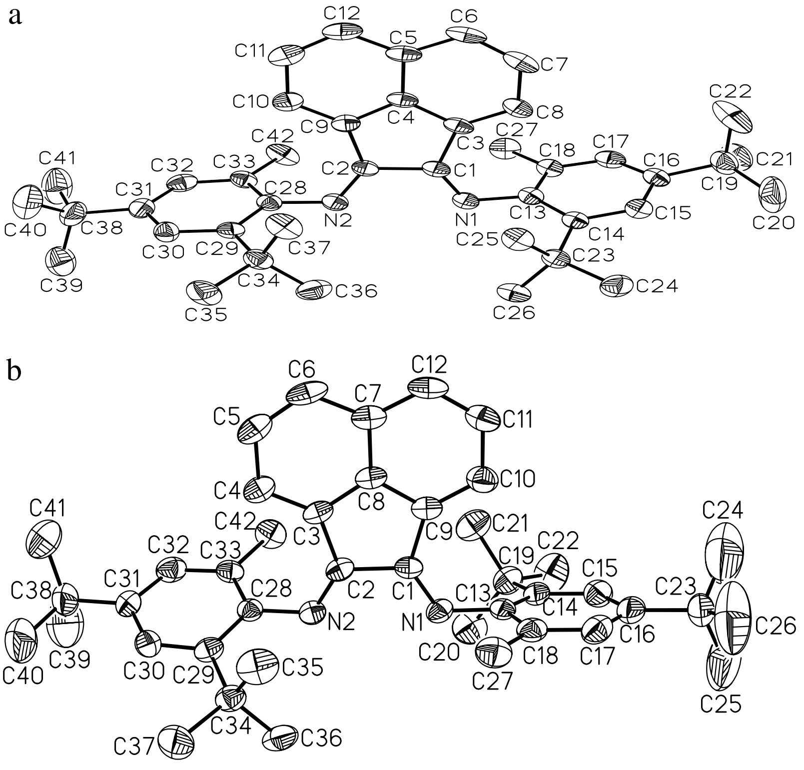


Fig. 2. X-ray structure of *meso*-ligand **3** (a) and *rac*-ligand **3** (b).

2.2. Polymerizations

On treatment with MAO, the unsymmetrical α-diimine nickel(II) complexes were used as catalysts for ethylene polymerization as shown in Table 1. Complex **1** was known and certain aspects of the polymerization behavior have been previously reported by us [22]. Complex **1**/MAO afforded

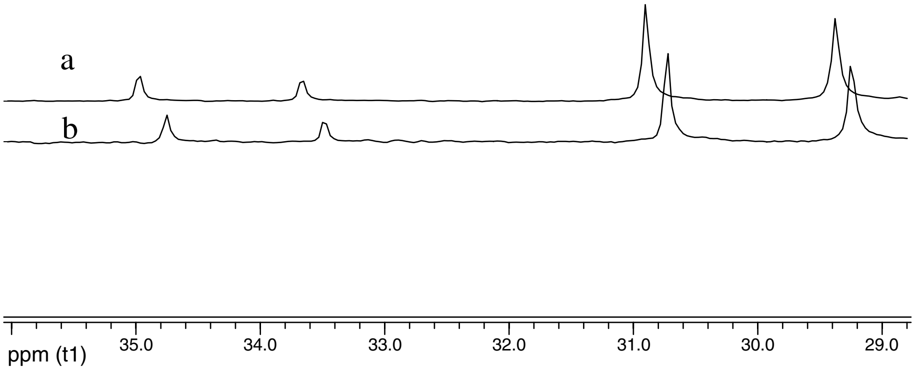


Fig. 3. ^{13}C NMR spectra of *rac*-ligand **3** (a) and *meso*-ligand **3** (b).

Table 1
The results of ethylene polymerization with unsymmetrical α-diimine nickel(II) catalysts[a]

Run no.	Catalyst	T_p (°C)	Productivity × 10^{-5} (g PE/mol Ni h)	M_w[b] × 10^{-4}	PDI[b]	Branch/1000 C[c]
1	**1**	−8	2.4	3.2	4.0	0
2	**2**	−20	3.4	39	2.5	0
3	**2**	20	5.2	20	2.9	43.6
4	**2**	40	3.1	12	4.1	111.3
5[d]	**2**	20	2.0	19	4.2	n.d[e]
6	*rac*-**3**	−10	1.8	210	2.5	1.9
7	*rac*-**3**	5	2.1	167	2.3	16.0
8	*rac*-**3**	30	0.9	53	2.2	n.d
9	*meso*-**3**	−10	1.9	112	2.1	42.2
10	*meso*-**3**	5	1.9	105	2.4	56.0
11	*meso*-**3**	30	2.3	31	2.0	n.d

[a] Polymerization conditions: [Ni] = 2.0×10^{-4} mol/L, $n_{Al}/n_{Ni} = 800$, $P(C_2H_4) = 0.15$ MPa, $t_p = 1$ h, toluene used as solvent.

[b] Determined by GPC.

[c] Degree of branching (branching numbers of 1000 carbon atoms in polyethylene main chain) determined by ^{13}C NMR.

[d] The complex **2** was dissolved in dichloromethane for 4 days and then used as catalyst for ethylene polymerization.

[e] Not determined.

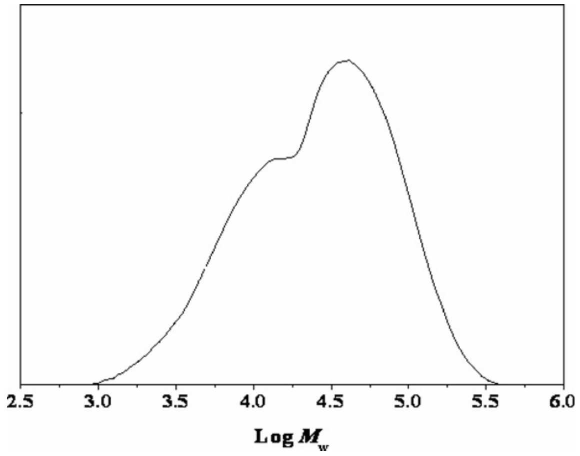
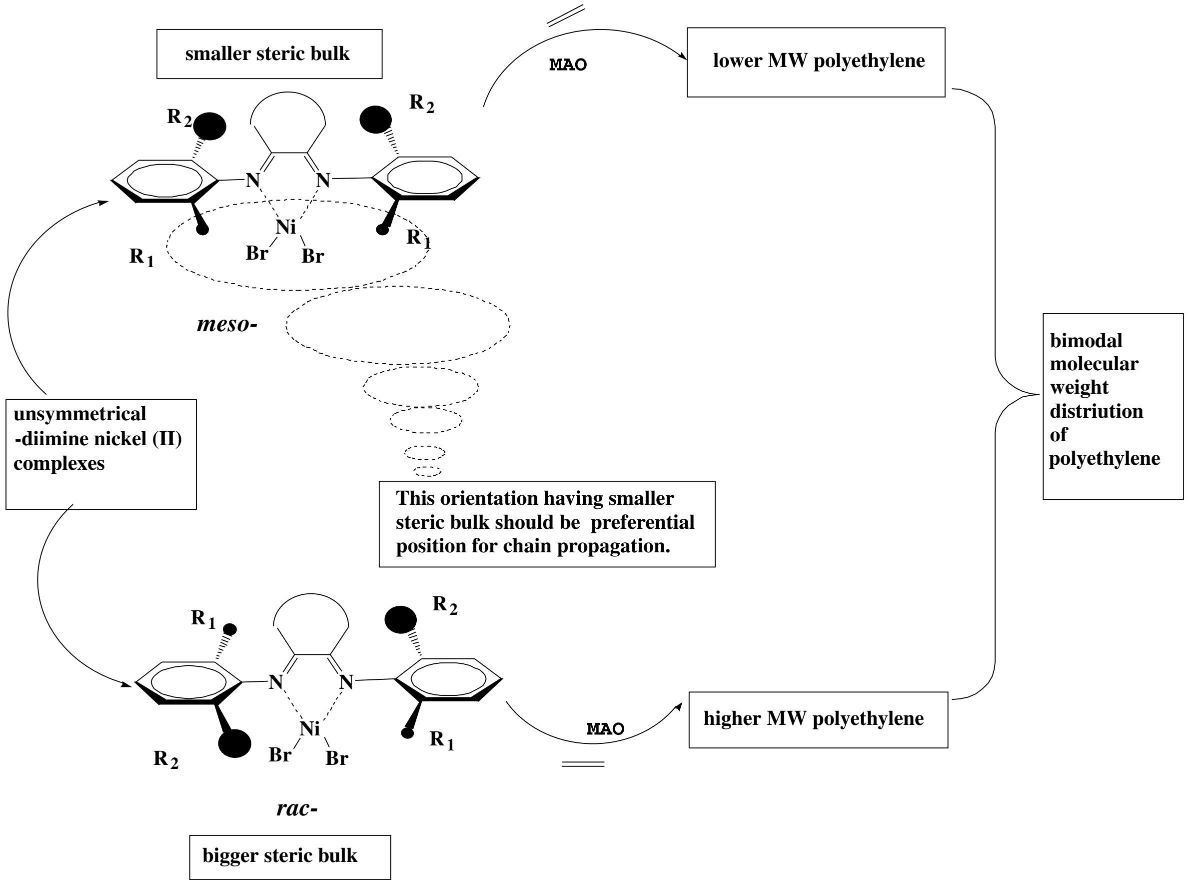


Fig. 4. GPC profile of polyethylene obtained from run **1** in Table 1.

polyethylene with bimodal molecular weight distribution at low polymerization temperature (Fig. 4). The possible mechanism of formation of bimodal molecular weight distribution polyethylene with unsymmetrical α-diimine nickel(II) catalysts was shown in Scheme 3. It is reasonable to postulate that the unsymmetrical α-diimine nickel(II) complexes possessed both *meso*- and *rac*-stereo-isomers, which might result in two active species with different steric bulk for ethylene polymerization under appropriate conditions. In *meso*-isomer, two bigger substituents (R_2) are oriented towards the virtual positions of the coordination plane in the same direction, which has bigger steric bulk for chain propagation compared with the opposite direction. Therefore, the orientation having smaller steric bulk should be the preferential position for chain propagation and provided polyethylene with low molecular weight. In *rac*-isomer, two bigger substituents (R_2) are in different directions. It is reasonable to believe that *rac*-isomer has bigger steric bulk for chain propagation than *meso*-isomer, and can synthesize higher molecular weight polyethylene. Using



Scheme 3. Proposed mechanism of synthesis of polyethylene with bimodal molecular weight distribution by unsymmetrical α-diimine nickel(II) catalysts.

unsymmetrical α-diimine nickel(II) complexes containing *meso*- and *rac*-isomers for ethylene polymerization, it is evident that bimodal molecular weight distribution polyethylene can be yielded. When we used 2,3-bis(α-naphthyl)-butanediimine nickel(II) dibromide to catalyze ethylene polymerization, polyethylene with bimodal molecular weight distribution was obtained [23].

In apparent contrast with the above discussion, the complex **2**/MAO afforded polyethylene with narrow molecular weight distribution (approximately 2) at low polymerization temperature, which strongly suggested a single active species catalyst [24]. Raising polymerization temperature, however, the molecular weight distribution of the produced polyethylene broadened. Fig. 5 shows the evidence for a bimodal distribution of polyethylene obtained by complex **2** (Table 1, run **4**). A possible explanation of the peculiar behavior was that only *rac*-**2** (*rac*-isomer of complex **2**) was obtained when ligand **2** was reacted with (DME)NiBr$_2$, since the *rac*-isomer of ligand **2** was the main product as detailed in Section 4. The similar results were observed in previous papers [19,25]. Moreover, the rate of conversion from *rac*-**2** to *meso*-**2** (*meso*-isomer of complex **2**) was so slow that there was only one active species at low

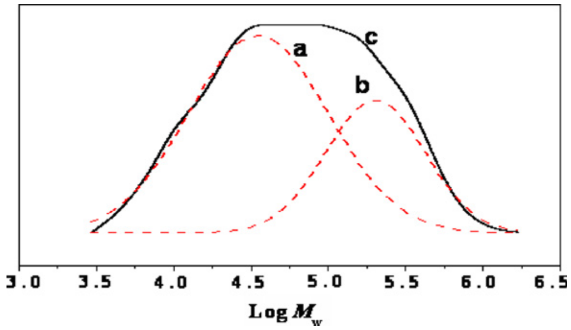


Fig. 5. GPC profiles of polyethylene samples obtained from run 4 (b) and run 7 (a) in Table 1.

polymerization temperature. As the increase of polymerization temperature, the rate of conversion from *rac*-**2** to *meso*-**2** was increased, and then there were two active species in the catalytic system, and leaded to the molecular weight distribution of polyethylene broadened. In addition, the effect of aged time of complex **2** on molecular weight distribution of produced polyethylene was also investigated. The complex **2** was dissolved in dichloromethane for 4 days and used as catalyst for ethylene polymerization in the presence of MAO. The result was displayed in Table 1. Extending the time of aging, interestingly, the molecular weight distribution of the produced polyethylene broadened from 2.9 to 4.2 (run **3** and run **5**, in Table 1). As shown in Fig. 1, the *rac*- and *meso*-isomers in ligand **2** could interconvert and got to a ca. 1:1 after 2 days. We supposed that the two isomers in complex **2** have the similar tendency as the two isomers of ligand **2,** though a detailed NMR analysis was precluded by the paramagnetic nature of Ni(II) atoms. After 4 days of aging in dichloromethane, the two isomers in complex **2** got to a certain ratio. As a result, the complex **2**/MAO showed two active species and the molecular weight distribution of polyethylene was broadened.

In order to demonstrate the hypothesis that the steric-bulk difference between *meso*- and *rac*-isomer could be the responsibility for bimodal molecular weight distribution, *meso*-**3** and *rac*-**3** were, respectively, activated by MAO for ethylene polymerization. As shown in Table 1, these catalysts show high activity for ethylene polymerization. It is interesting that molecular weight of polyethylene produced by *rac*-**3**/MAO was significantly higher than that produced by *meso*-**3**/MAO under the same polymerization conditions. In addition, the molecular weight distribution of the obtained polyethylene was narrow (M_w/M_n was about 2.0) and single-modal as displayed in Fig. 6, which implied that the resultant polyethylene from *meso*-**3** or *rac*-**3** was synthesized by single active species [24]. These results suggested that the conversion between *meso*-**3** and *rac*-**3** was difficult at the range of the polymerization temperature from −10 °C to 30 °C because of the sterically bulky substituents. Moreover, using *meso*-**3** and *rac*-**3** together for ethylene polymerization, it is evident that bimodal molecular weight distribution polyethylene is obtained. Moreover, it is worth mentioning that the products produced by *meso*-**3** and *rac*-**3** were branched polyethylene as the same as that synthesized by symmetrical α-diimine nickel catalysts [17].

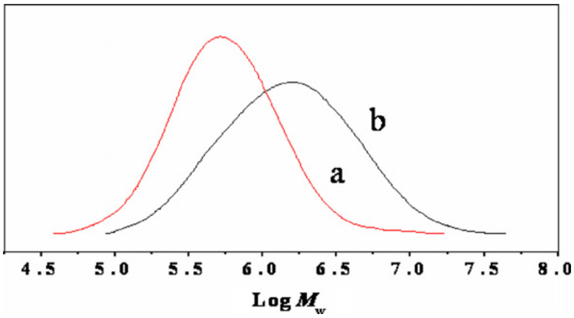


Fig. 6. GPC profiles of polyethylene samples obtained from run 6 (b) and run 9 (a) in Table 1.

3. Conclusion

The reaction of diketone and aniline with different steric bulk ortho substituents on aromatic ring can obtain *meso*- and *rac*-isomers in α-diimine ligands. Both isomers can interconvert owing to the rotation of aromatic ring and the conversion rate depends on steric bulk of the substituents and temperature. The corresponding unsymmetrical α-diimine nickel(II) complexes could possess both *meso*- and *rac*-isomers, and produce two active species with different steric bulk when combined with MAO. The molecular weight of polyethylene produced by *rac*-catalyst was significantly higher than that produced by *meso*-catalyst under the same polymerization conditions. Using unsymmetrical α-diimine nickel(II) catalysts including *meso*- and *rac*-isomers for ethylene polymerization, bimodal or broad molecular weight distribution polyethylene can be obtained in appropriate polymerization conditions.

4. Experimental section

4.1. Materials

Polymerization-grade ethylene and extra-pure-grade nitrogen were further purified before feeding into the reactor through a DC-IB gas purification instrument. Toluene was refluxed over metallic sodium for 48 h and distilled under nitrogen atmosphere before use. MAO was prepared by first the controlled reaction of trimethylaluminum (TMA) with H_2O from $Al_2(SO_4)_3 \cdot 18H_2O$ dispersed in toluene for several hours, then filtration, and finally evaporation under vacuum to give white solids. Complex **1** was prepared according to modified literature procedures [22]. α-Diimine ligands **2**, **3** and complex **2**, *rac*-**3** and *meso*-**3** were prepared according to modified literature procedures [13,26].

4.2. Synthesis of (ArN=C(An)–C(An)=NAr) (Ar=2-isopropyl-6-methylphenyl)

Acenaphthenequinone (2.1 g, 12 mmol) and 2-isopropyl-6-methylaniline (4.2 mL, 25 mmol) were stirred for 24 h at 25 °C in 60 mL of ethanol containing 1 mL formic acid. The precipitated orange solid was collected by filtration and dried. The cure product was recrystallized from a mixed solvent of petroleum ether/ethyl acetate 1:1 to give the pure ligand **2**, yield 2.3 g, 46%. ^{13}C NMR ($CDCl_3$, selected resonances): δ 161.2 (*C*=N), 148.5 (ipso-*C*(Ar)), 136.1 (*C*(Ar)–CH(CH_3)$_2$), 124.6 (*C*(Ar)–CH_3), 29.3 (*C*H(CH_3)$_2$), 24.5, 23.5 (CH(*C*H$_3$)$_2$), 18.3 (Ar*C*H$_3$). A second isomer (<20%) is detected: ^{13}C NMR ($CDCl_3$, selected resonances): δ 161.0 (*C*=N), 29.6 (*C*H(CH_3)$_2$), 24.1, 23.3 (CH (*C*H$_3$)$_2$). NMR monitoring at 25 °C shows slow isomerization. Anal. Calcd. for $C_{32}H_{32}N_2$: C, 86.44; H, 7.25; N, 6.30. Found: C, 86.19; H, 7.31; N, 6.21.

4.3. Synthesis of (ArN=C(An)–C(An)=NAr) (Ar=2,4-di-tert-butyl-6-methylphenyl)

2,4-Di-*tert*-butyl-6-methylaniline was synthesized adapting the literature procedure [27] by nitration of 3,5-di-*tert*-butyltoluene affording selectively 2-nitro-3,5-di-*tert*-butyl-toluene, and subsequent reduction. Then acenaphthenequinone (0.42 g, 2.3 mmol) and 2,4-di-*tert*-butyl-6-methyl-aniline (1.01 g, 4.6 mmol) were allowed to react for 48 h in 50 mL boiling acetic acid. After cooling at 25 °C, the precipitated orange solid was collected by filtration and dried, yield 0.85 g, 60%. The cure product was recrystallized from a mixed solvent of petroleum ether/ethyl acetate 1:1 to obtain the pure ligand **3**, yield 0.78 g. Anal. Calcd. for $C_{42}H_{52}N_2$: C, 86.25; H, 8.96; N, 4.79. Found: C, 86.78; H, 8.59; N, 4.54. Two isomers were detected in the condensation product by ^{13}C NMR characterization in ca. 1:1 ratio. Separation was achieved via column chromatography (20 g silica gel, petroleum ether/toluene 1:1). According to the X-ray diffraction analysis, the first eluted isomer was *rac*-isomer and the second eluted isomer was *meso*-isomer. *Meso*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, 2H), 7.35 (d, 2H), 7.18 (t, 2H), 7.08 (d, 2H), 6.58 (d, 2H), 1.96 (s, 6H, ArC*H*$_3$), 1.35 (s, 18 H, *p*-C (C*H*$_3$)$_3$), 1.28 (s, 18 H, *o*-C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$, selected resonances): δ 159.3 (*C*=N), 146.0 (*ipso*-*C* (Ar)), 34.8 (*p*-*C* (CH_3)$_3$), 33.6 (*o*-*C* (CH_3)$_3$), 30.8 (*p*-C (*C*H$_3$)$_3$), 29.3 (*o*-C (*C*H$_3$)$_3$), 17.8 (Ar*C*H$_3$). *rac*-Isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, 2H), 7.32(d, 2H), 7.18 (t, 2H), 7.06 (d, 2H), 6.57 (d, 2H), 1.94 (s, 6H, ArC*H*$_3$), 1.32 (s, 18 H, *p*-C (C*H*$_3$)$_3$), 1.26 (s, 18 H, *o*-C (C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$, selected resonances): δ 160.2 (*C*=N), 146.0 (*ipso*-*C* (Ar)), 35.1 (*p*-*C* (CH_3)$_3$), 33.7 (*o*-*C* (CH_3)$_3$), 30.9 (*p*-C (*C*H$_3$)$_3$), 29.5 (*o*-C (*C*H$_3$)$_3$) ppm, 17.8 (Ar*C*H$_3$).

4.4. Synthesis of complex 2

(DME)$NiBr_2$ (0.8 g, 2.58 mmol) and ligand 2 (1.1 g, 2.58 mmol) were combined in a Schlenk flask under a nitrogen atmosphere. CH_2Cl_2 (40 mL) was added, and the reaction stirred for 48 h at 25 °C. The supernatant liquid was removed, and the product washed with 2 × 10 mL of ether and dried in vacuum. The product was isolated as an orange–brown solid (1.4 g, 70% yield). Anal. Calcd. for $C_{32}H_{32}N_2NiBr_2$: C, 57.96; H, 4.86; N, 4.22. Found: C, 57.74; H, 4.81; N, 4.21.

4.5. Synthesis of meso-3

The synthesis of *meso*-**3** was carried out according to complex **2**, using 0.26 g of *rac*-isomer of ligand **3** (0.45 mmol) and 0.14 g of (DME)$NiBr_2$ (0.45 mmol). Yield 0.25 g (69%) of an orange–red solid. Anal. Calcd. for $C_{42}H_{52}N_2NiBr_2$: C, 62.79; H, 6.52; N, 3.49. Found: C, 63.09; H, 6.68; N, 3.63.

4.6. Synthesis of rac-3

The synthesis of *rac*-**3** was carried out according to complex **2**, using 0.39 g of *rac*-isomer of ligand **3** (0.67 mmol) and 0.21 g of (DME)$NiBr_2$ (0.67 mmol). Yield 0.30 g (56%) of an orange–red solid. Anal. Calcd. for $C_{42}H_{52}N_2NiBr_2$: C, 62.79; H, 6.52; N, 3.49. Found: C, 62.69; H, 6.48; N, 3.50.

4.7. Polymerization of ethylene

The polymerization runs were carried out under an extra-pure-grade nitrogen atmosphere in 100 mL glass flask equipped with a magnetic stirrer. The MAO, toluene were introduced into the reactor, and then saturated with 0.15 MPa ethylene, at last the nickel complex dissolved in dichloromethane was added. The polymerizations were terminated by the addition of 10 wt.% HCl in ethanol.

The polymers were washed with ethanol and dried in a vacuum at 60 °C to constant weight.

4.8. Characterization

Gel-permeation chromatography (GPC) of polymers was performed on a Water 150C at 135 °C and 1,2,4-trichlorobenzene as solvent. The columns were calibrated with narrow molecular weight distribution polystyrene standards. ^{13}C NMR spectra of polyethylene samples were recorded at 120 °C in a 10 mm tube using an INOVA 500 MHz spectrometer. The samples were dissolved in *o*-dichlorbenzene/benzene-d_6 to form a 15 wt.% solution. The chemical shift value (30.00 ppm) of main backbone methylene was used as an internal standard. The samples were obtained by removing the aluminum co-catalyst through the addition of HCl acidified ethanol and subsequent filtration of the polymerization products.

Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 613619) for *meso*-ligand **3** and (CCDC No. 613620) for *rac*-ligand **3**. Copies of this information may be obtained free of charge by mail (The Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB$_2$ 1EZ, UK), by fax: +44 1223 336033, by e-mail (deposit@ccdc.cam.ac.uk), or on the web (http://ccdc.cam.ac.uk).

Acknowledgments

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